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54 A method for the production of oligomers

57 A method for the production of basically linear oligomers of alkenes with between 4 and 6 carbon atoms on the basis of alkenes or hydrocarbon flows that contain alkenes in a heterogeneous nickel-containing catalyst in an adiabatically operated reactor at temperatures of between 20 and 300 °C and pressures values of between 1 and 100 bar by processing a first partial discharge flow from the reactor onto the oligomers and by returning the second partial flow together with fresh alkene or a fresh hydrocarbon flow that contains such alkenes back to the reactor.

Description

This invention concerns a method for the production of basically linear oligomers of alkenes with between 4 and 6 carbon atoms on the basis of alkenes or a hydrocarbon flow that contains such alkenes on a heterogeneous nickel-containing catalyst in an adiabatically operated reactor at temperatures of between 20 and 300 °C and at pressure values of between 1 and 100 bar.

Alkenes with between 2 and 6 carbon atoms and their mixtures and particularly alkene with 4 carbon atoms are available in large quantities from FCC units as well as steam crackers. The respective C₄-section, i.e., the mixture of butene and butanes, are particularly well suited for the production of oligomers and particularly of octenes and dodecenes after the iso-butene has been separated. Through a hydroformylation and subsequent hydration to form the respective alcohols, octenes as well as dodecenes can be used for the manufacture of softening agents, for example.

In that respect, the degree of branching of the softening agent alcohol has a major effect on the softener properties. The degree of branching is described with the ISO-index that indicates the average number of methyl branchings in a fraction of isomeric compounds from hydrocarbon chains, particularly of alkenes and of alcohols derived from them in this case. For example, n-octene adds 0, methyl heptene adds 1 and dimethyl hexene adds 2 to the ISO-index. In other words:

A lower ISO-index indicates that the molecules in the respective fraction are more linear. The ISO-index gets lower with an increasing linearity and this indicates higher yields in the oxation and better properties for the thus produced softening agents.

The older German patent application with the file number 199 10 103.5 describes a method for the oligomerization of C₆-alkenes by reacting reaction mixtures that contain C₆-alkenes on a solid bed catalyst containing nickel, in which case it is important that no more than 30% by weight of the C₆-alkenes in relation to the reaction mixture is converted. Unreacted C₆-alkenes can be separated from the oligomeric products and can be returned to the reaction process.

Furthermore, from WO-A 99/25668 is known a method for the production of basically linear octenes and dodecenes, in which hydrocarbon flows that contain 1-butene and/or 2-butene and butane are reacted on a heterogeneous catalyst that contains nickel. In that connection, the butane separated from the reaction mixture and unreacted butene are returned to the oligomerization reaction in such a manner that the maximum oligomer content in the unreacted reaction mixture never exceeds 25% by weight at any point in the reactor.

The oligomerization of low-molecular alkenes is generally accompanied by a noticeable heat of reaction. Furthermore and under adiabatic conditions, the reaction mixture removes practically the whole reaction heat from the reactor in the case of a reaction on a heterogeneous catalyst. This indicates that the reactor throughput and thus also the conversion per time unit are a function of the amount of heat that must be removed from the reactor. Accordingly, the expert meters the alkene flow in the reactor and sets the remaining reaction parameters in such a manner that the desired oligomer concentration is found in the exiting product flow after the alkene flow

has passed once through the reactor ("in a straight passage"). He normally establishes this optimization again for each individual case and he optimizes the above-mentioned parameters with the help of many initial tests. Under these circumstances, however, one achieves just one utilization rate that is not yet satisfactory.

Accordingly, the task of this invention consists in the development of a heterogeneously catalytic adiabatic method for the production of alkene oligomers in which the reactor temperature can be controlled in a more flexible manner than in similar known methods with a simultaneous high yield and high product selectivity.

In accordance with the invention, this task is solved with a method for the production of basically linear oligomers of alkenes with between 4 and 6 carbon atoms based on alkenes or on hydrocarbon flows that contains such alkenes on a heterogeneous nickel-containing catalyst in an adiabatically operated reactor and at temperatures of between 20 and 300 °C and at pressure levels of between 1 and 100 bar, i.e., by processing a first partial flow from the reactor discharge onto the oligomers and by returning the second partial flow together with a hydrocarbon flow that contains fresh alkene or fresh alkenes into the reactor.

In this application, "oligomers" means dimers, trimers and higher products - based on the joint bedding of alkenes with between 4 and 6 carbon atoms - with up to 18, preferably 12 and particularly preferred 8 carbon atoms.

This invention is based on the knowledge that a mixing of the oligomeric mixture formed in the method with initial alkenes without oligomers is of no significance for the activity level exhibited by the nickel catalyst, for the overall yield and particularly for the method selectivity.

Suitable catalysts consist of catalysts that generally contain Nickel and are known to affect a minor oligomer branching: See, for example, *Catalysis Today*, 6, 329 (1990), particularly pages 336-338, as well as the references listed in WO-A 95/14647 and in the older German patent application with file number 199 57 173.2 regarding prior art, in which case reference is made here explicitly regarding the catalysts.

The following oligomerization catalysts can be listed as Ni-catalysts samples in which the nickel generally occurs in the oxidic form:

- Nickel on silicon dioxide,
- Nickel on silicon dioxide-aluminum oxide,
- Nickel on silicon dioxide-aluminum oxide-layer silicates such as mica and oxides of aluminum, particularly montmorillonite,
- Nickel on zeolite carriers such as mordenite, faujasite, zeolite X, zeolite Y, zeolite ZSM-5 or other zeolites of the ZSM-type, zeolites with a MCM-41 structure or a CZS-1 structure,
- Nickel on aluminum oxide, possibly together with anions of particularly inorganic acids such as sulfuric, phosphoric and boric acid,
- Nickel on zirconium oxide that has been treated with acids such as sulfuric acid, phosphoric acid or boric acid,

- NiO/ZrO₂/SO₄/SiO₂-systems,
- Nickel on sulfated titanium oxide.

The oligomerization catalysts that contain nickel and are used here in accordance with the invention are hereinafter called "Ni-catalysts".

According to a preferred example of the method in accordance with the invention, the oligomerization is performed in the liquid phase and with the use of the Ni-catalysts described and claimed in WO-A 95/14647 and in the older German patent application with file number 199 57 173.2. Reference is made here explicitly to these documents and their information regarding method and Ni-catalysts is considered incorporated here.

The catalytically active mass of the Ni-catalysts described in WO-A 95/14647 basically consists of nickel oxide, silicon oxide, titanium oxide and/or zirconium oxide and possibly of aluminum oxide, i.e., without considering contaminants that were introduced through initial or process chemicals during the production of the Ni-catalysts. These Ni-catalysts contain between 10 and 70% by weight nickel oxide, between 5 and 30% by weight titanium dioxide and/or zirconium dioxide, between 0 and 20% by weight aluminum oxide and the rest to reach 100% by weight consists of silicon dioxide. They are obtained by precipitating the Ni-catalyst mass at a pH-value of 5-9 by adding an aqueous solution that contains nickel nitrate to an alkali water glass solution that still contains titanium and/or zircon dioxide. The thus obtained Ni-catalyst mass is then filtered, dried and tempered at between 350 and 650 °C.

The Ni-catalysts described in the older German patent application with file number 199 57 173.2 mainly consist of aluminum oxide that was coated with a nickel compound and a sulfur compound, in which case the completed Ni-catalyst exhibits a molar ratio between sulfur and nickel of 0.25:1 to 0.38:1.

The Ni-catalysts used in accordance with the invention are preferably arranged on a solid bed and thus consist of solid pieces such as tablets (5 mm x 5 mm, 5 mm x 3 mm, 3 mm x 3 mm), rings (7 mm x 7 mm x 3 mm, 5 mm x 5 mm x 2 mm, 5 mm x 2 mm x 2 mm) or strands or star strands (1.5 mm diameter, 3 mm diameter, 5 mm diameter). The above sizes and body types represent just examples and do in no way restrict the object of this invention.

The method in accordance with the invention is performed by reacting the alkenes with between 4 and 6 carbon atoms (hereinafter called "alkenes") or their mixtures with alkanes, preferably in the liquid phase, on the above-mentioned Ni-catalyst.

Suitable and preferred alkenes consist of simple unsaturated butenes, pentenes and hexenes, particularly 1-butene, 2-butene, 1-pentene, 2-pentene, 1-hexene or 3-hexene by themselves.

The method in accordance with the invention permits the use of material flows with a normal alkene content of between 5 and 100% by weight, preferably of between 30 and 100% by weight and particularly preferred of between 50 and 100% by weight.

The method in accordance with the invention is particularly suited for the reaction of alkenes that are present in a mixture with alkane, in which case each of the alkenes and alkanes has 4 carbon atoms. Such suitable C₄-hydrocarbon flows may consist of mixtures with the following composition:

Butane	10 to 90% by weight
Butene	10 to 90% by weight

in which case the butene fraction may have the following composition:

1-butene	1 to 50% by weight
cis-2-butene	1 to 50% by weight
trans-2-butene	1 to 99% by weight
iso-butene	1 to 5% by weight

The so-called Raffinate II is considered a particularly preferred material to be used. This is a C₄-hydrocarbon mixture that contains butene and is obtained from the C₄-section from crackers after the separation of higher unsaturated hydrocarbons such as dialkenes, particularly 1,3-butadiene, or acetylene and subsequently the iso-butene contained in it. The following shows a typical composition of Raffinate II:

iso- and n-butane	26% by weight
iso-butene	1% by weight
1-butene	26% by weight
trans-2-butene	31% by weight
cis-2-butene	16% by weight

Butadienes and compounds that contain sulfur and oxygen such as alcohols, aldehydes, ketones or ethers can be removed from the C₄-hydrocarbon flows through a hydration or adsorption on molecular sieves as indicated in DE-A 39 14 817.

The oligomerization reaction is generally run at temperatures of between 30 and 280 °C, preferably of between 30 and 140 °C and particularly preferred of between 40 and 130 °C and at a pressure of generally between 1 and 300 bar, preferably of between 5 and 100 bar and particularly preferred of between 20 and 70 bar. In that regard, the pressure is selected appropriately in such a manner that the hydrocarbon mixture is present in an above-critical manner and particularly in the liquid state at the adjusted temperature.

The reactor generally consists of a cylindrical reactor in which the Ni-catalyst is placed; as an alternative, it is also possible to use a cascade with several and preferably with two such reactors arranged in series.

The Ni-catalyst can be arranged on a single or on several solid Ni-catalyst beds in the reactor or in individual reactors. Although it is preferred to use the same Ni-catalysts in all reactors of the cascade, it is also possible to use different Ni-catalysts in the individual reactors of the cascade.

Furthermore, different reaction conditions with respect to pressure and/or temperature within the above-mentioned pressure and temperature ranges can be set in the individual reactors of the reactor cascade.

The liquid reaction mixture may pass, for example, from the top to the bottom through the solid Ni-catalyst bed in the reactor or reactor cascade.

The single reactor and the reactor cascade for the reaction on the solid bed of the Ni-catalyst described and used in accordance with the invention will hereinafter be summarized under the term "solid bed reactor".

From a technical point of view, an adiabatic reaction or operation refers to a reaction or operation, in which the whole reaction heat is absorbed by the reaction mixture and is discharged with it from the reactor, i.e., with the exception of the part of the reaction heat that is transferred to the outside through a natural heat conduction and heat dissipation process.

From a technical point of view and in contrast to the above, an isothermal reaction or operation forces the removal of the reaction heat from the reactor with cooling and thermostat devices in a targeted manner and in addition to the natural heat conduction and dissipation process. In that regard, it is practically impossible to avoid that a - negligibly small - part of the reaction heat is transferred outward with the reaction mixture.

As an alternative to the above-mentioned solid bed reactors, the process in accordance with the invention can also be run in other reactors that are known to the expert as suitable for such heterogeneously catalyzed reactions, i.e., stirrer tanks or loop-type bubble reactors (see M. Baerns, H. Hoffmann, A. Renken, Chemical Reaction Technology, Thieme Verlag, Stuttgart 1987, page 237 and following).

In such processes, the conversion rate to form oligomers generally varies between 10% and 100% and preferably between 50% and 100% in relation to the alkenes used in the reaction.

After leaving the single- or multi-reaction zone, the raw product flow is divided into a first and a second partial product flow.

The first partial flow is in a generally known manner and preferably by distillation processed onto the formed oligomers. In this regard, rests of unreacted alkenes and of the possibly accompanying alkanes are separated as purge flow.

The purge flow generally contains alkene rests of between 5 and 20% by weight and is of little values to serve as a basic material for organic syntheses. Accordingly, it is used for other applications such as a cracking process which may again produce alkenes that can be used in the method in accordance with the invention.

The purge flow may also be partially or completely returned to the reactor. Because of its low content of reactive alkene, its effect consist of increasing the material flow through the reactor and to thus dilute the alkene and contribute to the temperature control in the reactor. Furthermore, it becomes easier to control the upper limit for the oligomer content in the product flow.

The second product flow is returned to the process with practically no changes to its composition. The temperature of the second partial product flow can be set to the desired value prior to supplying it to the reactor using known devices such as heat exchangers.

Since methods such as those in accordance with the invention are generally optimized for materials of a specific type and composition, it is generally necessary to bring the alkene percentage content in the second partial product flow again close to or actually to the initial value at the reactor inlet. In accordance with the invention, this is achieved by supplying the partial flow with fresh alkenes that may be mixed with one or several alkanes.

In view of the desired oligomer yield and selectivity and the thus required temperature setting on the reactor inside, the expert may perform initial tests to easily determine the ratio between the fresh alkene flow and possibly returned percentage content of the purge flow and the second partial flow prior to the feed into the reactor.

Furthermore, it is possible to return the unreacted alkene with between 4 and 6 carbon atoms that was recovered when processing the first partial flow together with possible accompanying alkanes to the reactor.

The feed of the second partial product flow and the fresh alkene flow into the reactor can be achieved such that the flows are piped into the reactor simultaneously and possibly through separate pipes or after a previous mixing.

Prior to their metering into the reactor, the temperature of each flow or of the mixture of the material flows can be established with devices such as heat exchangers that are known for this purpose.

When the Ni-catalyst is arranged on several solid beds in the reactor, the mixed material flows can be piped into the reactor in a divided form and at several points such as upstream of a first solid bed in the flow direction of the reaction mixture and/or between individual solid Ni-catalyst beds. When using a reactor cascade, for example, it is possible to pipe the whole quantity of the mixed material flows to the first cascade reactor or by way of several feed pipes to the individual cascade reactors as was described for the case of an individual reactor.

With the method in accordance with the invention, one obtained oligomer contents of between 5 and 100% by weight, preferably of between 10 and 60% by weight and particularly of between 15 and 30% by weight in relation to the whole product flow. To achieve such an oligomer content, it is generally necessary to set a weight ratio of 0.5 to 10, preferably of 1 to 7 and particularly preferred of 1 to 4 between the return flow and the freshly supplied hydrocarbon flow, in which case this information relates to the stationary state of the reaction system.

Although the method becomes uneconomical due to the excessively large return flow quantity required when selecting a very low oligomer content, there does not exist a lower limit for the oligomer content in the reaction mixture. Accordingly, a lower limit of 10% by weight in the unreacted reaction mixture prior to its dividing is generally set.

The method in accordance with the invention permits the expert to flexibly affect the heat development in the reactor, since he can select the ratio between the feed flows to the reactor freely and over a broad range. Furthermore, he is able to particularly adjust the temperature of the second partial flow in a targeted manner.

Furthermore and using the method in accordance with the invention, it is possible to lower the heating of the material flow through the reactor ("temperature rise") close to the point of a quasi-isothermal reaction, thus achieving an even better control of the reactor temperature.

The method in accordance with the invention will be explained here with the following examples.

Examples

Figure 1 shows a schematic representation of a device used to run the process in accordance with the invention. The reaction is assumed to be in the stationary state already. Fresh alkene is supplied to the reactor (3) through (1) and heat exchanger (2). The raw product flow in pipe (4) is partly and without processing piped to the reactor through pipe (4a). The other part of the raw product flow is piped through (4b) to column (5), where it is separated into the oligomeric products (6) and the head product (7). The head product (7) is completely or partly transferred outward from the process through (7b), in which case a possibly remaining part is through (7a) and together with the fresh alkene (1) and the partial flow from (4b) piped to the reactor by way of the heat exchanger.

A) Ni-catalysts

Ni-catalyst I

A material of the composition 50% by weight NiO, 12.5% by weight TiO₂, 33.5% by weight SiO₂ and 4% by weight Al₂O₃ was processed to form 3 mm star strands according to and as described in WO-A 95/14647.

Ni-catalyst II

A material of the composition 8.9% by weight Ni, 1.6% by weight S and the rest to 100% Al₂O₃ was produced in the form of 3 mm star strands according to and as described in the older German patent application with the file number 199 57 173.2.

Ni-catalyst III

A material of the composition 50% by weight NiO, 12.5% by weight TiO₂, 33.5% by weight SiO₂ and 4% by weight Al₂O₃ was processed to a non-formed spray granulate (particle size 100-350 µm) according to and as described in WO-A 95/14647.

B) Hydrocarbons with 4 to 6 carbon atoms used here

A Raffinate II of the following composition was used:

iso-butane	3% by weight
n-butane	15% by weight
iso-butene	2% by weight
1-butene	30% by weight
trans-2-butene	32% by weight
cis-2-butene	18% by weight

The C₆-mixture used here had the following composition:

1-hexene	<0.1% by weight
trans-2-hexene	<0.1% by weight
cis-2-hexene	<0.1% by weight
trans-3-hexene	86.2% by weight
cis-3-hexene	12.2% by weight
2-methyl pent-2-ene	1.1% by weight
pentene	0.5% by weight

C) Oligomerizations

Example 1

Raffinate II as the feed was reacted on a solid bed of 83 g Ni-catalyst filled to a height of 22 cm in a tube reactor (inside diameter of 28 mm, length of 50 cm) in a straight pass or with a return. Further test parameters and the test results are summarized in Table 1.

Table 1

	T [°C]	Feed [g/h]	Return [g/h]	Yield [% by weight]	C ₈ -Selectivity [%]
Without return	80	40	0	28.1	69.7
	80	66	0	24	72.1
	80	115	0	17.1	77.9
With return	80	40	820	27.6	70
	80	62	870	23	73.7
	80	100	840	17.9	77.3

Explanation of the symbols shown in the Table:

T: Reaction temperature

Return: Return of a partial flow containing an oligomer in accordance with the invention

Yield: Oligomer yield in relation to the whole raw product discharge

C₈-Selectivity: Percentage content of C₈-isomers (in this case) in the oligomers in the whole product flow

Example 2

Raffinate II as the feed was reacted on a solid bed of 95 g Ni-catalyst II filled to a height of 23 cm in a tube reactor (inside diameter of 28 mm, length of 50 cm) in a straight pass or with a return. Further test parameters and the test results are summarized in Table 2.

Table 2

	T [°C]	Feed [g/h]	Return [g/h]	Yield [% by weight]	C ₈ -Selectivity [%]
Without return	75	100	0	31.1	83.9
	85	80	0	34	83
	75	100	720	29	84.5
With return	85	80	710	32.5	83.5

Explanation of the symbols shown in the Table as in Example 1.

Example 3

A quantity of 20 g Raffinate II as the feed was reacted with 2 g Ni-catalyst III for 16 hours and at 80 °C in a stirrer tank. The oligomer yield in relation to the whole raw product discharge was 19% by weight; the percentage content of C₈-isomers in these oligomers was 75.1%.

A quantity of 67 g Raffinate II as the feed per hour was reacted with 30 g Ni-catalyst III in a fluidized bed at 37 °C, in which case the feed passed through from the bottom and was thus suspended to a height of 29 cm. The return rate was 960 g/h. The oligomer yield in relation to the whole raw product discharge was 23.4% by weight; the percentage content of C₈-isomers in these oligomers was 73.9%.

Example 4

A C₆-mixture as the feed was reacted on a solid bed filled with 880 g Ni-catalyst I to a height of 75 cm in a tube reactor (inside diameter of 48 mm, length of 90 cm) in a straight passage or with a return. Further test parameters and the test results, particularly the selectivity with respect to C₁₂-isomers, are summarized in Table 3.

Table 3

	T [°C]	Feed [g/h]	Return [g/h]	Yield [% by weight]	C ₈ -Selectivity [%]
Without return	50	528	0	22.9	80.7
	50	142	0	36.8	75.6
	50	45	406	46.1	73.8
With return	50	163	812	28.4	77.4

Explanation of the symbols shown in the Table as in Example 1.

Patent claims

1. A method for the production of mainly linear oligomers with alkenes with 4 to 6 carbon atoms based on alkenes or on hydrocarbon flows that contain alkenes on a heterogeneous nickel-containing catalyst in an adiabatically operated reactor at temperatures of between 20 and 300 °C and pressure values of between 1 and 100 bar, **characterized by the fact that** a first partial flow from the reactor discharge is processed onto the oligomers and the second partial flow with the fresh alkene or the fresh hydrocarbon flow that contains such alkenes is returned to the reactor.
2. A method in accordance with claim 1, characterized by the fact that the unreacted alkenes with between 4 and 6 carbon atoms that were recovered during the processing of the first partial flow and possibly the alkanes are partially or completely returned to the reactor.
3. A method in accordance with claims 1 or 2, characterized by the fact that the first partial flow is equal to between 1 and 50% by weight of the reactor discharge.
4. A method in accordance with claims 1 or 2, characterized by the fact that the first partial flow is equal to between 1 and 20% by weight of the reactor discharge.
5. A method in accordance with claim 1 or 2, characterized by the fact that the first partial flow is equal to between 1 and 10% by weight of the discharge.
6. A method in accordance with one of claims 1 through 5, characterized by the fact that the hydrocarbon flows that contain alkenes have at least one alkene from the group of n-butene, n-pentene, n-hexene.
7. A method in accordance with one of claims 1 through 6, characterized by the fact that the oligomer percentage content in the reactor discharge varies between 1 and 80% by weight.
8. A method in accordance with claims 1 through 6, characterized by the fact that the oligomer percentage content in the reactor discharge varies between 10 and 50% by weight.
9. A method in accordance with claims 1 through 6, characterized by the fact that the oligomer percentage content in the reactor discharge varies between 15 and 25% by weight.
10. A method in accordance with one of claims 1 through 9, characterized by the fact that the weight ratio between the second partial flow and the fresh alkene or the fresh hydrocarbon flow that contains such an alkene varies between 1:1 and 50:1.
11. A method in accordance with one of claims 1 through 9, characterized by the fact that the weight ratio between the second partial flow and the fresh alkene or the fresh hydrocarbon flow that contains such an alkene varies between 2:1 and 20:1.
12. A method in accordance with one of claims 1 through 9, characterized by the fact that the weight ratio between the second partial flow and the fresh alkene or the fresh hydrocarbon flow that contains such an alkene varies between 5:1 and 20:1.

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Figure 1